

CHEMISTRY

PAPER—I

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

**Please read each of the following instructions carefully
before attempting questions**

There are **ELEVEN** questions divided under **SIX** Sections.

Candidate has to attempt **SIX** questions in all.

The **ONLY** question in Section—A is **compulsory**.

Out of the remaining **TEN** questions, the candidate has to attempt **FIVE**, choosing **ONE** from each of the other Sections B, C, D, E and F.

The number of marks carried by a question/part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the Question-cum-Answer (QCA) Booklet must be clearly struck off.

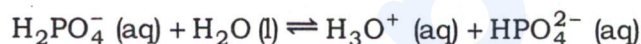
Answers must be written in **ENGLISH** only.

(Compulsory Section)

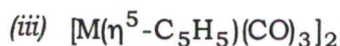
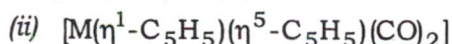
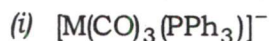
1. Answer **all** of the following questions :

5×10=50

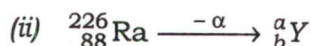
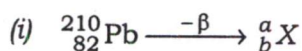
- (a) Zinc blende and wurtzite are two different naturally occurring minerals, having same cation/anion in unary composition, but crystallizes in two different forms. Rationalize the observation with radius of cation (74 pm or 88 pm) and anion (184 pm).
- (b) Intensities of spin-forbidden transitions are greater for 4d- or 5d-series metal complexes than for 3d-series metal complexes. Explain it.
- (c) Phosphate ions are abundant in cells. The typical total phosphate concentration in a cell $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-]$ is $2.0 \times 10^{-2} \text{ M}$. What are the concentrations of HPO_4^{2-} and H_2PO_4^- at pH 7.40? (Given : pK_a for H_2PO_4^- ion is 7.20, which is very close to the normal pH in the body)



- (d) Find the concentration of added Ag^+ to just start precipitation of AgCl in a $1.0 \times 10^{-3} \text{ M}$ solution of NaCl , if K_{sp} of AgCl at 25°C is 1.0×10^{-10} .
- (e) Distinguish between iodometry and iodimetry with examples.
- (f) Give at least two examples of masking agents. How are they used in the estimation of Ca^{2+} ion, if the solution contains ions like Ni^{2+} or Ag^+ ? Explain with suitable equations.
- (g) Identify the first row transition metal in the following organometallic compounds obeying EAN rule :



- (h) Find the values of a and b in the following reactions of radioactivity :



Predict the position of the daughter element in the periodic table.

- (i) Account for the similar electronic spectra of Eu^{3+} complexes with various ligands and the variation of electronic spectra of Am^{3+} complexes as the ligand is varied.
- (j) Calculate the minimum moles of urea required for complete precipitation of 0.02 mol of Fe^{3+} as $\text{Fe}(\text{OH})_3$.

SECTION—B

Attempt *any one* question.

2. (a) Which one, SrCl_2 or CdCl_2 , follows fluorite structure? Explain with suitable pictorial diagram. [Ionic radii (in pm) : Sr^{2+} —113; Cd^{2+} —97; Cl^- —181] 10
- (b) The spectrum of $[\text{Cr}(\text{NCS})_6]^{3-}$ has a very weak band near 16000 cm^{-1} , a band at 17700 cm^{-1} with $\epsilon_{\text{max}} = 160\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, a band at 23800 cm^{-1} with $\epsilon_{\text{max}} = 130\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, a very strong band at 32400 cm^{-1} . Assign these transitions, using selection rule considerations. 10
- (c) Nickel and palladium both form complexes of the general formula $\text{M}(\text{PR}_3)_2\text{Cl}_2$. The nickel(II) compound is paramagnetic, whereas the palladium(II) compound is diamagnetic.
- (i) Explain the magnetic properties of these compounds.
- (ii) How many isomers of each compound are expected? 10
3. (a) Among the mixed metal oxides NiCr_2O_4 and NiCo_2O_4 , one of the oxides is structurally dissimilar to MgAl_2O_4 . Explain. 10
- (b) $\text{cis-PtCl}_2(\text{PEt}_3)_2$ is stable in benzene solution. However, small amount of free triethylphosphine catalyzes establishment of an equilibrium with the *trans*-isomer :
- $$\text{cis-PtCl}_2(\text{PEt}_3)_2 \rightleftharpoons \text{trans-PtCl}_2(\text{PEt}_3)_2$$
- For the conversion of *cis* to *trans* in benzene at 25°C , $\Delta H^\circ = 10.3\text{ kJ mol}^{-1}$ and $\Delta S^\circ = 55.6\text{ J mol}^{-1}\text{ K}^{-1}$.
- (i) Calculate the equilibrium constant for this isomerization.
- (ii) Which isomer has higher bond energy? Explain briefly.
- (iii) Why is free triethylphosphine necessary to catalyze the isomerization? 10

- (c) (i) Give a balanced equation for the reaction of lanthanoids with aqueous acid. Justify your answer.
- (ii) Name the two lanthanoids that have greatest tendency to deviate from the usual positive oxidation state and correlate this deviation with electronic structure.

10

SECTION—C

Attempt *any one* question.

4. (a) Suggest indicators in the following titration :

0.1 M ethylenediamine and HCl

Given :

$$\left. \begin{array}{l} K_{b1} = 8.5 \times 10^{-5} \\ K_{b2} = 2.7 \times 10^{-8} \end{array} \right\} \text{ at } 25^\circ \text{C}$$

(Assume the quantitative formation of mono- and di-protonated species)

10

- (b) What is homogeneous precipitation? Discuss its advantages over direct precipitation.

10

- (c) Explain the working principle of redox indicators with example.

10

5. (a) Suggest why the pertechnetate ion is red, permanganate ion is purple and manganate ion is green. Describe the most likely absorption that gives rise to colours in these ions. Also include energy level sketch showing how *d*-orbitals on metals interact with oxide orbitals to form molecular orbitals.

10

- (b) Describe the experimental procedure for gravimetric estimation of nickel in grams per litre with necessary calculation steps.

10

- (c) How is standard electrode potential (E°) of $\text{Mn}^{7+}/\text{Mn}^{2+}$ determined experimentally through potentiometric titration of standard KMnO_4 versus Mohr's salt solution?

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SECTION—D

Attempt *any one* question.

6. (a) Consider the following equilibrium :



Find the compounds *I* and *J*, and draw the crystal field splitting diagram (with labels and filled electrons of orbitals) of silver complex (*I*).

10

- (b) Derive an equation having relation between hydrolysis constant and degree of hydrolysis of a salt of weak base and strong acid. 10
- (c) Derive Nernst equation for the cell potential of silver-copper cell. 10

7. (a) An aqueous solution of CuSO_4 and CdSO_4 was combined with excess KCN solution and then H_2S (gas) was passed through the solution mixture to obtain an insoluble yellow-coloured precipitate. Find the products and give reasons, along with equations, as to why only one of the metal compounds is formed as precipitate. 10

(b) Phenol ($\text{C}_6\text{H}_5\text{OH}$) is a weak organic acid. Suppose 0.515 g of the said compound is dissolved in enough water to make 125 mL of the solution. The resulting solution is titrated with 0.123 M NaOH. [Given : K_a (Phenol) $= 1.3 \times 10^{-10}$ at 25 °C]

(i) What is the pH of the original solution of phenol?

(ii) What are the concentrations of all of the following ions at the equivalence point?

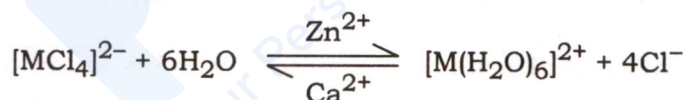


(iii) What is the pH of the solution at the equivalence point? 20

SECTION—E

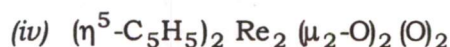
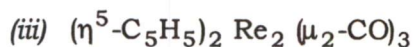
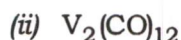
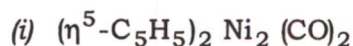
Attempt *any one* question.

8. (a) In the following equilibrium



find M assuming that the magnetic moments of $[\text{MCl}_4]^{2-}$ and $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ are 3.87 BM and ~ 4.1 BM respectively. What will be the colour of these complexes, and why is the equilibrium shifted upon addition of Zn^{2+} or Ca^{2+} ions to the reaction medium? 10

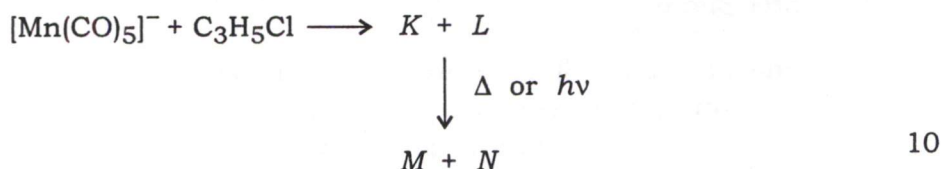
(b) Among the following organometallic compounds, which one will have the maximum number of bonds between the two metal centres, and a least number of *d*-electrons at the metal centre?



- (c) Calculate the half-life period of radium-226, if 0.001 kg of it emits 3.7×10^{10} alpha particles per second. 10

9. (a) How is isotope dilution method used to determine the amount of an element present in a sample? 10

- (b) Find the products (K to N) in the following reaction and show the metal to ligand bond connectivities, only for organometallic species :



- (c) For each of the compounds $[\text{Co}(\text{bipy})_3]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$, answer the following :

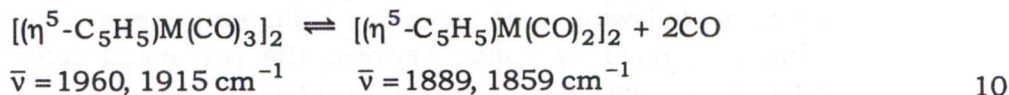
- (i) Find the ground state term symbol.
- (ii) Use the Tanabe-Sugano diagram to identify the predicted spectral bands.
- (iii) Do you expect broad or narrow absorption bands in the visible and UV regions?
- (iv) Sketch an MO energy level diagram for each. 10

SECTION—F

Attempt *any one* question.

10. (a) The amount of C-14 isotope in a piece of wood is found to be one-sixth of its amount present in a fresh piece of wood. Calculate the age of the wood. Given that half-life of C-14 = 5577 years. 10

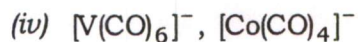
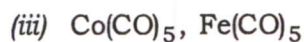
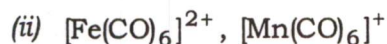
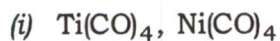
- (b) The stretching frequency values of both starting material and the products are given below in the reversible reaction. Find M which belongs to the principal quantum number of $n = 5$ and draw both the structures :



- (c) Barium ion estimation can be done using EDTA directly, whereas aluminium ion estimation cannot be performed directly with EDTA. Why? 10

11. (a) Explain the construction and working principle of Geiger-Müller counter with diagram. 10

(b) Find the correct pair(s) of stable organometallic compounds and rationalize the answer :



10

(c) One of the rarest minerals cristobalite of silica forms basic core unit similar to that of one of the allotropes of carbon. Draw this basic core unit of silica and provide a rationale as to why carbon analogue does not form such network type structure.

10

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